this rock powder no line of lead was obtained until the current exceeded seven amperes. This could be due to the fact that in the complex matrix some unknown ingredient depressed the emission lines of lead. The usual practice of compounding comparison standards was therefore not advisable, and the method of addition was followed.

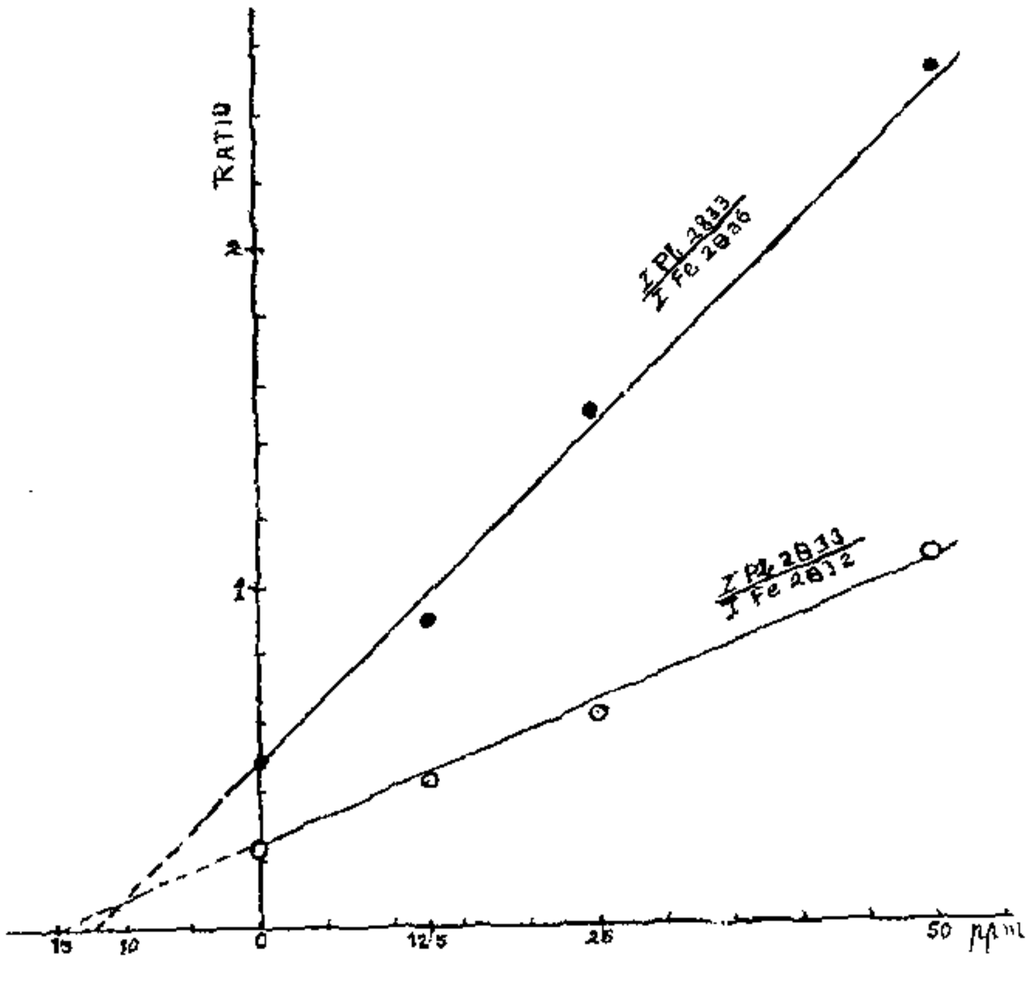


FIG. 1

Three standards were prepared by adding $Pb_2O_3$ to the rock powder. The concentration of lead in the standards was $(x + 0{\cdot}00125)$, $(x + 0{\cdot}0025)$, and $(x + 0{\cdot}005)$ %, where $x$% is the concentration of lead in the rock sample.

The arc separation was 4 mm, and the centre of the arc was focused with the Zeiss-system on the slit of Q 24-Zeiss Spectrograph, the slit width being 10 μ. The arc was run at 45 volts and 9 amperes. Ten seconds after starting the arc, an exposure of ten seconds was given in each case. This short exposure, almost immediately after starting the arc, was given to minimise the effect of self-reversal of Pb-lines.

The photographic response-relative intensity curve was constructed with Fe lines, with relative intensities given by Ahrens and Taylor.[2] Pb 2833 was used for analysis, with Fe lines 2832 and 2836 as internal standards.

The lead concentration in the rock sample as obtained from the graph is 14 ± 1 ppm.

Dept. of Physics, S. J. KHAMBATA.
St. Xavier's College, M. D. MIRANDA.
Bombay, *March* 24, 1966.

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## CHEMICAL EXAMINATION OF THE LEAVES OF *CASSIA JAVANICA* LINN.

VARIOUS *Cassia* species have been the subjects of chemical investigation because of their tanning and medicinal properties.[1] *Cassia javanica* Linn. is an ornamental tree with light pink flowers and is reported[2] to be a native of Java and Sumatra. When the present work on the leaves was in progress Khorana et al.[2] reported the presence of 0·25 to 0·4% of free anthraquinones and 1·3% of combined anthraquinones in these leaves, but the isolation of only rhein and its glucoside. In the present study besides these, two more anthraquinones, chrysophanol and aloe-emodin are found to be present in small amounts. In addition four flavonoids have also been isolated.

The air-dried powdered leaves collected locally in July-August were exhaustively extracted with hot alcohol. The alcohol extract was concentrated under reduced pressure and water added. Some solid separated which was found to contain polymeric leucoanthocyanidins. The aqueous alcoholic filtrate was extracted with petroleum ether to remove waxes and chlorophyll and then successively with ether and ethyl acetate respectively. 400 mg. of the ether extract (yield 1·2%) was chromatographed over silica gel column and the following five fractions were obtained on elution; fraction (*a*) with ethyl acetate-benzene (1 : 3), 40 mg.; (*b*) with ethyl acetate-benzene (1 : 1), 30 mg.; (*c*) with ethyl acetate, 120 mg.; (*d*) with acetone and acetone-methanol (1 : 1), 100 mg.; and (*e*) with methanol, 30 mg.

Fraction (*a*) crystallised from ethyl acetate-petroleum ether as pale yellow needles, m.p. 278–280° and was identified to be kæmpferol by m.p., U.V. and visible spectra and confirmed by m.m.p., co-chromatography with the authentic sample and preparation of tetraacetate, m.p. 182–184°. Fraction (*c*) crystallised from methanol as pale yellow prisms, m.p. 225–227° and was found to be glycosidic in nature. After acid hydrolysis with 7% sulphuric acid the aglycone and the sugar moiety were identified to be kæmpferol and rhamnose respectively by comparison with authentic samples. To locate the site of glycosidic linkage in the glycoside it was fully methylated with dimethyl sulphate in anhydrous acetone solution containing suspended potassium carbonate. The resulting methyl ether on acid hydrolysis gave kæmpferol-5 : 7 : 4'-trimethyl ether, m.p. 149–150°; $\lambda_{max.}$ (in methanol) 260, 308 and 355 mμ; with aluminium chloride, $\lambda_{max.}$ 267,

330 and 410–15 mμ, a bathochromic shift of 55–60 mμ was observed in the band I which is characteristic of a free 3-hydroxyl group. Acetate of the glycoside had m.p. 157–158°. The data agreed completely with that recorded for kæmpferol-3-rhamnoside,[3] and so the glycoside was considered to have the same constitution.

*Fraction (b) contained another compound* admixed with the above two. This was separated by preparative thin-layer chromatography on silica gel using ethyl formate-toluene-formic acid mixture (4 : 5 : 1). The compound gave colour reactions and spectral characteristics of flavonoids but it could not be identified due to lack of material.

Fraction (d) was a mixture of anthraquinones and very small amount of flavonoids. *The separation of these was achieved by* preparative thin-layer chromatography over silica gel using ethyl formate-toluene-formic acid mixture (4 : 6 : 1). Three bands of anthraquinones appeared distinctly while a small amount remained *at the origin*. The above three bonds were scrapped off from several plates and eluted with acetone. Each fraction was purified by repeating the process. These were identified as chrysophanol, rhein and aloe-emodin on *the basis of absorption* spectra in the U.V. and visible regions and co-chromatography on paper and thin-layer (*silica gel*) using a number of solvent systems. Fraction (*e*) was glycosidic in nature. On acid hydrolysis it gave rhein as the aglycone and glucose as the sugar moiety as identified by co-chromatography with authentic samples. The above anthraquinone derivatives were found to be present in very small amounts as compared to the findings of Khorana *et al.*[2]

The ethyl acetate extract indicated the presence of leucoanthocyanidin in good yield. *To identify it the leaves were separately* extracted in the cold with acetone and the extract was worked up in the manner indicated above. Addition of petroleum ether to the dried ethyl acetate extract precipitated the *leucoanthocyanidin admixed with small amount* of kæmpferol-3-rhamnoside. The leucoanthocyanidin was converted into its flavylium salt which after purification was identified to be pelargonidin chloride by colour reactions, visible *spectra and co-chromatography with an* authentic sample of pelargonidin chloride.

This association of anthraquinone derivatives with flavonoids seems to be common in *Cassia* species. Kæmpferol-3-rhamnoside and leucopelargonidin are the major constituents of the leaves of *C. javanica*.

Department of Chemistry, S. P. BHUTANI.
University of Delhi, S. S. CHIBBER.
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## *CHEMICAL EXAMINATION OF THE LEAVES OF GLIRICIDIA MACULATA* (H.B. AND K.) STEUD.

*Gliricidia maculata* (H.B. & K.) Steud. [syn. *G. sepium* (Jacq.) Walp.] is a tall shrub cultivated in South India as a green manure and as a hedge plant.[1] The seeds were examined for their proximate constituents and the seed oil for its chemical constants by Earle *et al.*[2] The presence of coumarin, o-coumaric acid and melilotic acid was detected paper chromatographically in the leaves by Griffiths *et al.*[3] The flowers were found to contain quercetin 3-glucoside by Nair and Sankarasubramanian.[4] In the present investigation the leaves were subjected to a complete study and the results are reported here.

The dried leaves were successively extracted with warm petroleum ether, ether and alcohol. Chromatography of the unsaponifiable matter of the petroleum ether extract on alumina yielded a colourless waxy substance, m.p. 79·3–79·7°. It analysed for $C_{26-28}$ $H_{54-58}O$, did not show evidence for unsaturation and formed an acetate m.p. 62–4°. These properties showed that it is "ceryl alcohol" (Piper *et al.*[5]). The ether extract of the leaves did not yield any worthwhile material.

The alcoholic extract was concentrated, *diluted with* water and extracted successively with benzene, ether and ethyl acetate. The last (ethyl acetate) extract gave a very hygroscopic solid which was purified by taking up in water and extracting with butanol. Treatment of the butanol concentrate with petroleum ether yielded a pale yellow solid which crystallised from alcohol as minute short prisms, m.p. 218–26°. Colour reactions showed that it was a flavonoid glycoside. Hydrolysis with hot 7% sulphuric acid yielded an aglycone which from its m.p. (276–78°), analysis, colour reactions, spectral data and the melting point of its acetate (178–81°) was identified as kæmpferol (3, 5, 7, 4'-tetrahydroxyflavone). The sugars were identified as D-glucose and L-rhamnose by paper chromatography.